



Short communication

Ultra-high-rate all-solid pseudocapacitive electrochemical capacitors

Han Gao^a, Yen-Jui Ting^b, Nazir P. Kherani^{a,b}, Keryn Lian^{a,*}^a Department of Materials Science and Engineering, University of Toronto, Toronto, Ontario, Canada^b Department of Electrical and Computer Engineering, University of Toronto, Ontario, Canada

H I G H L I G H T S

- ▶ A solid redox supercapacitor with ultra-high rate performance was demonstrated.
- ▶ Mo_xN electrodes and a solid polymer electrolyte form thin/flexible supercapacitors.
- ▶ Due to redox reactions, a capacitance of 1 mF cm⁻² was delivered at 100 Vs⁻¹.

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A solid pseudocapacitive electrochemical capacitor (EC) enabled by a polymer electrolyte and molybdenum nitride electrodes has been developed and has demonstrated ultra-high rate performance. The solid EC can deliver 1 mF cm⁻² at 100 Vs⁻¹ and achieve a 10 ms time constant. This not only exceeds its liquid EC counter-part but also greatly surpasses a similar EC with titanium nitride electrodes as well as nanocarbon based electrochemical double layer capacitors.

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1. Introduction

Although electrochemical capacitors (EC) are high power energy storage devices, their application in the microelectronics industry has by far been limited due to their moderate charge–discharge rates compared to electrolytic capacitors as well as their large and bulky form factors. Only recently, ECs with ultra-high rate capability (up to 400 Vs⁻¹ and 120 Hz filtering) have been reported [1–6]. ECs store energy via electrochemical double layer capacitance (EDLC) or via Faradic charge transfer reactions (also known as pseudocapacitance). While EDLC originates from the rapid adsorption/desorption of ions, pseudocapacitance involves slower electrochemical oxidation–reduction reactions but can store 10–100 times more charge than EDLC [7]. To date, ultra high-rate ECs are all based on EDLC utilizing advanced carbon nano-materials such as onion-like nanocarbon [1] or graphene [2,3] in liquid electrolyte systems or using graphite in advanced polymer electrolytes [5,6]. These thin and highly conductive nanocarbon

electrodes possess a readily accessible surface, which enables high rate performance. To further improve the energy density of ECs, metal-based pseudocapacitive electrodes could be exploited. High-rate pseudocapacitive ECs (also known as redox supercapacitors) so far have been limited to expensive RuO₂ electrodes [8,9]. Transition metal nitrides, such as V_xN, Mo_xN, and TiN, have been reported to possess pseudocapacitive properties, and could potentially become low-cost alternatives to RuO₂ [10–13]. To develop ECs with thin and flexible form factors and with multi-cell/single packaging, polymer electrolytes are key enablers since they can act, at the same time, as separators and ionic conductors without leakage issues. The most mature polymer electrolytes are Nafion® and its derivatives [14]. Although they have been reported as electrolytes for ECs [15,16], they are highly sensitive to humidity at ambient operating temperatures [14,17]. Heteropoly acids (HPAs) [18] are promising solid proton conductors. Excellent rate and stability have been demonstrated for two common HPAs, silicotungstic acid (SiWA, H₄SiW₁₂O₄₀) and phosphotungstic acid (PWA, H₃PW₁₂O₄₀), immobilized in a polyvinyl alcohol (PVA) matrix [5,6,17,19]. Based on a solid-polymer electrolyte composed of SiWA, PVA, and H₃PO₄ (henceforth referred to as SiWA–H₃PO₄–PVA), we have developed all-solid ECs reaching rates as high as 20 Vs⁻¹ with graphite EDLC

* Corresponding author.

E-mail address: keryn.lian@utoronto.ca (K. Lian).

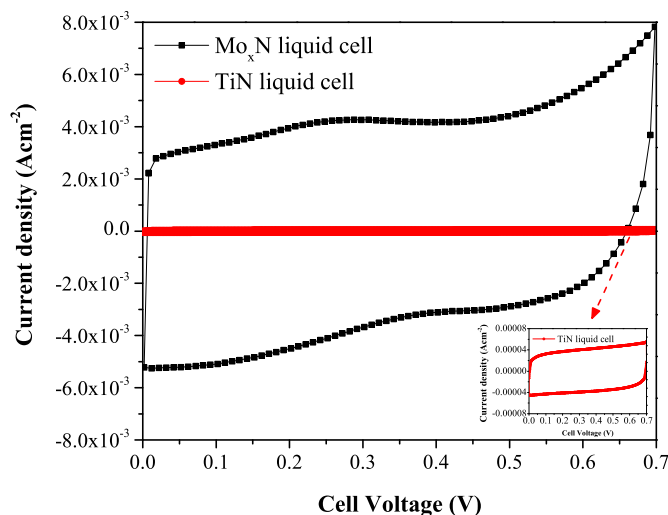


Fig. 1. CVs of liquid Mo_xN EC cell and liquid TiN EC cell (also shown as inset) with 0.5 M H_2SO_4 aqueous electrolyte at sweep rate of 1 Vs^{-1} .

electrodes [5]. Although these solid EDLC devices exhibited high-rate performance, their capacitance was relatively small. It is our objective to leverage metallic pseudocapacitive electrodes and a solid polymer electrolyte to develop ultra-high-rate, all-solid pseudocapacitive ECs. In this paper, we report a solid pseudocapacitive EC achieving 1 mF cm^{-2} cell capacitance at 100 Vs^{-1} with a 10 ms time constant. Due to pseudocapacitance, this is the highest area-specific capacitance at 100 Vs^{-1} reported to date for any EC device, liquid or solid.

2. Experimental

The SiWA– H_3PO_4 –PVA polymer precursor solution was prepared by mixing a poly(vinyl alcohol) (PVA, Aldrich MW = 145,000) solution with SiWA ($\text{H}_4\text{SiW}_{12}\text{O}_{40}$, Alfa Aesar), and Phosphoric acid (H_3PO_4 , Alfa Aesar) in a composition of 14.4% SiWA, 1.9% H_3PO_4 , 1.7% PVA, and 82% de-ionized water (all in wt.%). The electrodes were either molybdenum nitride on a titanium substrate (Mo_xN) or nitrided titanium (TiN).

Mo_xN electrodes were prepared by nitridation of electroplated Molybdenum oxides. Electroplating of molybdenum oxide was carried out on the titanium substrate using a CHI 660 potentiostat,

by sweeping an applied voltage from 0 to -0.75 V , cycling at a rate of 0.3 Vs^{-1} . In this 3-electrode plating system, the working electrode was titanium foil, the reference electrode was Ag/AgCl , and the counter electrode was a large area titanium sheet. The electroplating bath was prepared by dissolving $\text{MoNaO}_4 \cdot 2\text{H}_2\text{O}$ and Na_2SO_4 in de-ionized water to obtain a solution containing 0.4 M Na_2MoO_4 with a pH value of 2. Nitridation was carried out in a nitrogen atmosphere at 400°C using a tube furnace. For the TiN electrodes, titanium foils (Grade 2, Trinity Industries Inc.) were heated in a nitrogen environment similar to the electroplated Mo samples.

Solid-state EC devices were then assembled as reported in previous studies [5,6]. The electrolyte precursor solution was first coated onto both sides of the identical electrodes and dried in air. The coated electrodes were then laminated, with the electrolyte sandwiched in the middle, at 10–12 psi and 90°C for 15 min. The geometric area of the electrode was 0.8 cm^2 and the electrolyte thickness was in the range of 0.1–0.15 mm. For comparison, liquid EC devices utilizing a 0.15 mm thick filter paper soaked in a 0.5 M H_2SO_4 solution and sandwiched between the electrodes were also tested. The 0.5 M H_2SO_4 solution was selected to ensure the stability of Mo_xN . All EC devices were characterized using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) using a CHI 760D bipotentiostat. All electrochemical characterizations were conducted at ambient temperature. Scanning electron microscopy (SEM) micrographs were obtained using a Hitachi S-570 to study the morphologies of the Mo_xN and TiN surfaces. The surface roughness and coating thickness of the electrodes were also examined on a Zygo New View-100 optical profilometer.

3. Results and discussion

The pseudocapacitive electrode was a molybdenum nitride (Mo_xN , $x = 1\text{--}2$) film coated on a titanium substrate. The coating thickness was less than 100 nm. Its electrochemical behavior was compared with the TiN electrode. Fig. 1 shows the CV of a Mo_xN EC overlaid with the CV of a TiN EC in a 0.5 M H_2SO_4 aqueous electrolyte. The Mo_xN EC device exhibited an area-specific capacitance of 4.5 mF cm^{-2} at 1 Vs^{-1} , about 100 times greater than that of the TiN EC (inset).

To understand the origin of the excess capacitance of the Mo_xN EC, the surface morphologies of TiN and Mo_xN electrodes were examined by scanning electron microscopy (SEM). As shown in Fig. 2, both TiN and Mo_xN electrodes have a similar surface roughness. In addition, both TiN and Mo_xN cells were tested in an

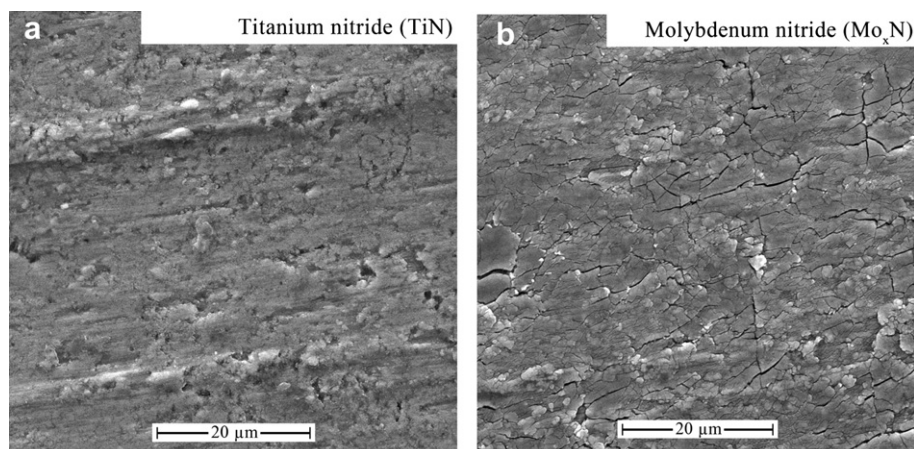


Fig. 2. SEM micrographs for (a) titanium nitride (TiN) electrodes and (b) molybdenum nitride (Mo_xN) on titanium substrate electrodes.

organic electrolyte (tetraethylammonium tetrafluoroborate in propylene carbonate) for their double layer capacitance. The resulting area-specific capacitance at 1 Vs^{-1} was in the range of $28\text{--}36 \mu\text{F cm}^{-2}$, implying comparable surface area for these two types of electrodes. Thus, the 100 times excess capacitance of Mo_xN is attributable to pseudocapacitance. Even though titanium nitride was reported to have pseudocapacitive behavior [12,13], the nitridation process did not add pseudocapacitance to the TiN electrodes. A detailed description of Mo_xN is beyond the scope of the current paper and has been reported elsewhere [20]. However, we did observe that the surface of Mo_xN exhibited a “mud-crack” morphology, as shown in Fig. 2, similar to that of pseudocapacitive RuO_2 [7].

The electrochemical performance of all-solid Mo_xN EC cells with $\text{SiWA-H}_3\text{PO}_4\text{-PVA}$ polymer electrolyte was characterized and further compared to a liquid Mo_xN EC cell with a $0.5 \text{ M H}_2\text{SO}_4$ aqueous electrolyte. Fig. 3a shows the CVs of both a solid and a liquid Mo_xN EC at a sweep rate of 1 Vs^{-1} . Both CVs exhibited near rectangular profiles, indicating good capacitive behavior. At this rate, the capacitance of the solid EC was about half of its liquid counterpart. A higher capacitance in the aqueous electrolyte than in the solid electrolyte was expected due to higher ionic accessibility

of the aqueous electrolyte to the electrode surface. However, the trend observed at higher sweep rates was different: Fig. 3b shows the CVs of the same EC cells at 10 Vs^{-1} . The CV profile of the solid Mo_xN EC remained rectangular and appeared less resistive than that of the liquid EC. Both solid and liquid Mo_xN ECs showed similar area-specific capacitance of 2 mF cm^{-2} , higher than the capacitance reported for high-rate EDLC devices [1–6]. To further investigate the high-rate performance of the solid Mo_xN EC, we pushed scan rates up to 100 Vs^{-1} . Fig. 4 shows the CVs of the solid Mo_xN EC at sweep rates of 10, 50, and 100 Vs^{-1} . The device delivered 1 mF cm^{-2} at 100 Vs^{-1} .

EIS was utilized to evaluate the frequency response of the solid Mo_xN EC. We used the approach by Taberna et al. [21] to separate the real part of the capacitance (C') from its imaginary part (C'') and plot them as a function of frequency (Fig. 5). C' represents the accessible capacitance per area of the device at the corresponding frequency, while C'' corresponds to energy dissipation by an irreversible process. The maximum of the C'' versus frequency curve represents a time constant at which a transition from resistive to capacitive behavior occurs. In Fig. 5a, at low frequency, C' of the liquid and the solid Mo_xN ECs approaches 5 mF cm^{-2} and 2.5 mF cm^{-2} , respectively, similar to the capacitance obtained from CV profiles (Fig. 3a). Although C' of the liquid Mo_xN EC was higher than that of the solid Mo_xN EC at low frequencies, this situation was reversed at frequencies higher than 10 Hz, where C' of the solid Mo_xN EC exceeded its liquid counterpart. This observation is in good agreement with the CV results in Fig. 3a and b. C'' of the liquid and solid Mo_xN ECs exhibited maxima at around 8 Hz and 100 Hz, respectively (Fig. 5b). These maxima translate to time constants of 125 ms for the liquid EC and 10 ms for the solid EC. The time constant of 10 ms for the solid Mo_xN EC was not only smaller than that of its liquid counterpart but was also smaller than that reported for high-performance onion-like nanocarbon electrodes in organic electrolytes [1] while exhibiting higher capacitance.

The equivalent series resistance (ESR) of the solid Mo_xN EC was extracted from the EIS spectra. The average ESR of the cells was $1.05 \pm 0.02 \Omega \text{ cm}^2$, combining the contributions of titanium substrate, Mo_xN film, and polymer electrolyte. The ionic conductivity of the $\text{SiWA-H}_3\text{PO}_4\text{-PVA}$ solid-polymer electrolyte was estimated to be 13 mS cm^{-1} , assuming no contribution of resistance from the Mo_xN film and the titanium substrate. Compared to the

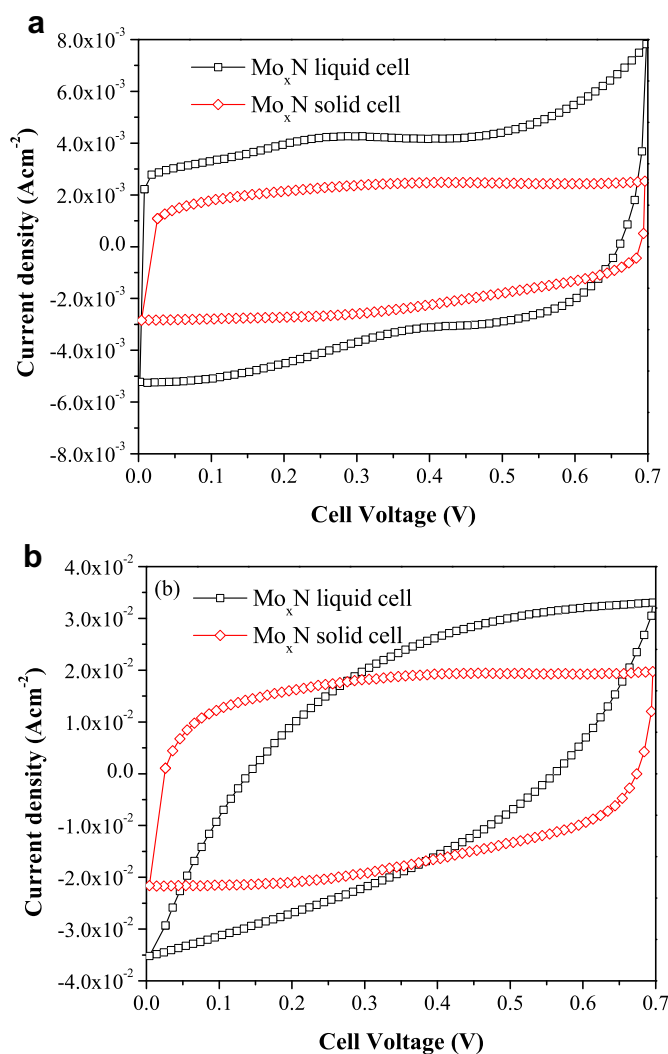


Fig. 3. CVs of liquid Mo_xN EC cell (Mo_xN electrode with $0.5 \text{ M H}_2\text{SO}_4$ aqueous electrolyte) and solid Mo_xN EC cell (Mo_xN electrode with $\text{SiWA-H}_3\text{PO}_4\text{-PVA}$ electrolyte): (a) at sweep rate of 1 Vs^{-1} ; (b) at sweep rate of 10 Vs^{-1} .

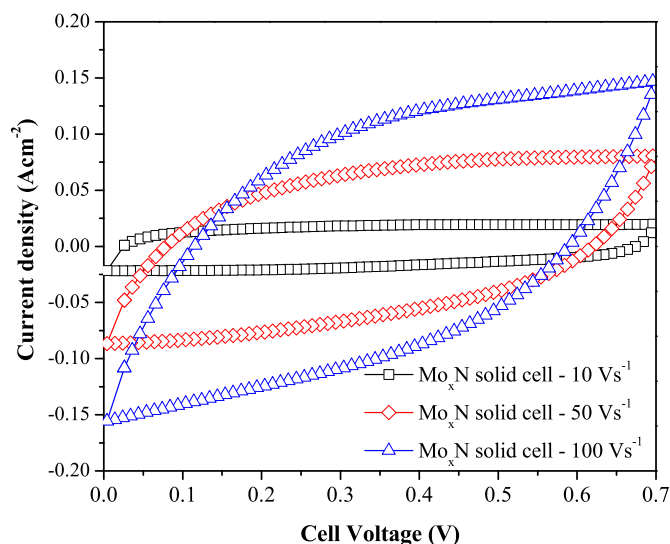


Fig. 4. CVs of solid Mo_xN EC cell (Mo_xN electrode with $\text{SiWA-H}_3\text{PO}_4\text{-PVA}$ electrolyte) at sweep rates of 10 Vs^{-1} (inner-most), 50 Vs^{-1} (middle), and 100 Vs^{-1} (outer-most).

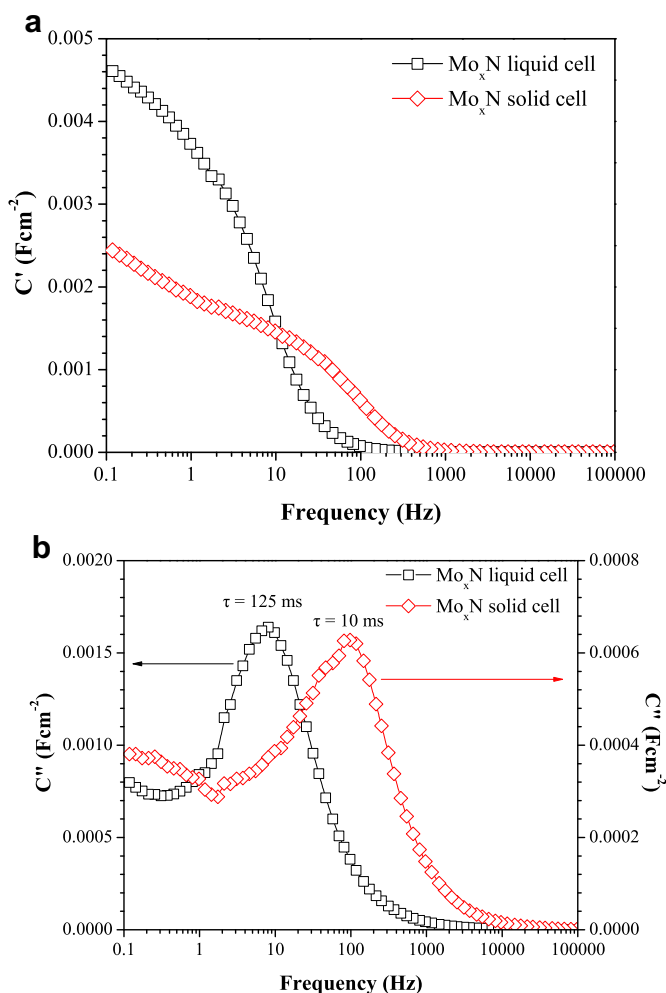


Fig. 5. Electrochemical impedance spectroscopy profiles showing the evolution of (a) the real part and (b) the imaginary part of capacitance vs. frequency from a solid Mo_xN EC cell (Mo_xN electrode with $\text{SiWA-H}_3\text{PO}_4\text{-PVA}$ polymer electrolyte) and a liquid Mo_xN EC cell (Mo_xN electrode with 0.5 M H_2SO_4 aqueous electrolyte).

ionic conductivity of solid SiWA (27 mS cm^{-1}) [18], the addition of 10% insulating polymer did not significantly decrease the conductivity of the solid electrolyte under ambient conditions.

The $\text{SiWA-H}_3\text{PO}_4\text{-PVA}$ solid-polymer electrolyte has demonstrated very promising performance and characteristics as electrolyte for high-rate ECs. The rate capability of an electrochemical capacitor depends on several factors: (a) the resistance of the electrodes, (b) the accessibility of the electrode surface to ions, (c) the ionic conductivity of the electrolyte and, (d) the electrode–electrolyte interface. In this study, we have employed Mo_xN electrodes on a Ti substrate which led to high electric conductivity. The thin and smooth deposition of Mo_xN allows the surface of the active material to be readily accessed by the electrolyte. The short and consistent proton conducting paths within a thin electrolyte film

enabled good ionic conductivity. Applying the polymer electrolyte precursor solution onto the electrodes first and then fusing them together achieved an intimate contact between electrodes and electrolyte. We have demonstrated that a minimized interfacial contact resistance of the thin and highly conductive electrolyte together with the highly conductive transition metal nitride are the keys to achieving the high rates and the small time constant in $\text{Mo}_x\text{N-SiWA-H}_3\text{PO}_4\text{-PVA}$ solid EC devices.

4. Conclusion

In this paper, we report preliminary results obtained leveraging both low cost pseudocapacitive Mo_xN electrodes and a solid-polymer $\text{SiWA-H}_3\text{PO}_4\text{-PVA}$ electrolyte to develop all-solid EC devices with ultra-high rate performance. For the first time, solid pseudocapacitive EC devices have been shown (i) to deliver a high charge of 1 mF cm^{-2} at an ultra-high rate of 100 Vs^{-1} , and (ii) to possess a 10 ms time constant. Further optimization of the solid $\text{SiWA-H}_3\text{PO}_4\text{-PVA}$ film for increased conductivity and stability is under way.

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References

- [1] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna, P. Simon, *Nature Nanotechnology* 5 (2010) 651–654.
- [2] J.R. Miller, R.A. Outlaw, B.C. Holloway, *Science* 329 (2010) 1637–1639.
- [3] K. Sheng, Y. Sun, C. Li, W. Yuan, G. Shi, *Scientific Reports* 2 (2012).
- [4] M.F. El-Kady, V. Strong, S. Dubin, R.B. Kaner, *Science* 335 (2012) 1326–1330.
- [5] H. Gao, K. Lian, *Journal of Power Sources* 196 (2011) 8855–8857.
- [6] H. Gao, K. Lian, *Journal of the Electrochemical Society* 158 (2011) A1371–A1378.
- [7] B.E. Conway, *Electrochemical Supercapacitors: Scientific Fundamentals and Technological Applications*, Plenum Press, 1999.
- [8] K. Lian, C. Li, R.H. Jung, J.G. Kins, U.S. Patent 5, 587, 872, 1996.
- [9] K. Lian, C.M. Li, *Electrochemistry Communications* 11 (2009) 22–24.
- [10] D. Choi, G.E. Blomgren, P.N. Kumta, *Advanced Materials* 18 (2006) 1178–1182.
- [11] T.-C. Liu, W.G. Pell, B.E. Conway, S.L. Roberson, *Journal of the Electrochemical Society* 145 (1998) 1882–1888.
- [12] S. Dong, X. Chen, L. Gu, X. Zhou, H. Xu, H. Wang, Z. Liu, P. Han, J. Yao, L. Wang, G. Cui, L. Chen, *ACS Applied Materials & Interfaces* 3 (2010) 93–98.
- [13] D. Choi, P.N. Kumta, *Journal of the Electrochemical Society* 153 (2006) A2298–A2303.
- [14] M. Maréchal, J.L. Souquet, J. Guindet, J.Y. Sanchez, *Electrochemistry Communications* 9 (2007) 1023–1028.
- [15] P. Staiti, M. Minutoli, F. Lufrano, *Electrochimica Acta* 47 (2002) 2795–2800.
- [16] P. Staiti, F. Lufrano, *Journal of the Electrochemical Society* 152 (2005) A617–A621.
- [17] H. Gao, H. Wu, K. Lian, *Electrochemistry Communications* 17 (2012) 48–51.
- [18] D.E. Katsoulis, *Chemical Reviews* 98 (1998) 359–388.
- [19] H. Gao, K. Lian, *Electrochimica Acta* 56 (2010) 122–127.
- [20] Y.-J. Ting, K. Lian, N. Kherani, *ECS Transactions* 35 (2011) 133–139.
- [21] P.L. Taberna, P. Simon, J.F. Fauvarque, *Journal of the Electrochemical Society* 150 (2003) A292–A300.